Traces of *copper* accelerate developer oxidation. This explains why developers prepared with distilled water often change more quickly than those prepared with ordinary water, as the distilled water frequently contains copper from the still. In addition sulphite itself contains 0·5 mg of copper per kg, which catalyses the oxidation reaction.

It is possible to prevent the copper from reacting with the developer by sequestering it with a complex forming agent. The best results are obtained with ethylenediamine-tetraacetic acid (disodium salt) (Trilon B) at a concentration of 2 g per litre. The amount of sulphite oxidized is then reduced to one-half. Unfortunately, *this sequestering agent is incompatible with hydroxylamine sulphate which it decomposes with the evolution of nitrogen.*(90)

558. Faults in the multilayer system

The superimposition of three emulsions differentially colour sensitized necessitates the *diffusion* of colour sensitizers and couplers being practically nil.

If the *colour sensitizers* diffuse from one layer to another the separating action of the system is partially destroyed. The diffusion of sensitizer may be even more pronounced if its molecule contains a shorter chain and if it is smaller. To increase this, other more complex nuclei must be attached to the benzene rings of the dye, such as fluorene groups. *The diffusion of sensitizers is always greatly reduced by the couplers dispersed in the emulsions.* In addition, their thinness enables drying to be rapid which still further limits the time in which diffusion is possible.

The *couplers* are, in principle, made non-diffusing by joining long chain groups to their molecules. However, Meyer and Ulbricht(91) have shown that a coupler although non-diffusing in gelatin (gel form) diffuses when it is in a solution of gelatin (sol form). Thus gelatin containing a non-diffusing coupler, coated on to an emulsion layer produces to some extent a coloured image in the latter by development.

559. Colour development faults

The colour developing agent, oxidized by the latent image, is converted to a *semi-quinone* which *diffuses* towards the neighbouring particles of coupler.

This diffusion is limited by the concentration of coupler. In actual films this concentration is generally adequate. If the coupler concentration is low, there will be a loss of sharpness. In addition, the diffusion of the oxidized developing agent is slowed down by sulphite which converts it to sulphonate.

The vertical *Eberhand effect* (para. 226c) due to local variations in the concentration of developer, its oxidation product, and the bromide byproduct, can effect the regions neighbouring high densities. In other words the image in a layer is to a greater or less extent influenced by the images in the other two layers, with possible reduction in the γ.

A multilayer system is subject to many possibilities of colour fog:(92)

1. *Emulsion fog*. Each of the 3 emulsions has its own fog level which results in a slight coloration if the 3-fog densities are not equal. This fault occurs in many ways from old material, for the speed of increase of fog for the three emulsions is rarely the same.

2. *Development fog*. Due to a lack of bromide, to protracted development, too high a temperature or the presence of an impurity in the solution.
3. *Oxidation fog* from the air (see para. 557).
4. *Oxidation fog by the bleach bath* of developer which has not been removed by washing, particularly in the lower (cyan) layer. By reaction of the oxidized developer and the coupler, a bluish fog is formed. This fog is lower around the perforations which are washed more efficiently than the rest of the film.
5. *Contact fog*. At the interface between the yellow filter, which contains colloidal silver (acting as development centres) a colour image is formed by the same mechanism as diffusion transfer (para. 406). The yellow and magenta layers may be stained in this way.
6. *Background stain* due to incomplete elimination of the colour sensitizers, the filter layer or the anti-halo layer.

560. Correction of colour casts

A colour cast of a developed film may be due to a negative defect, a printing error, an exposure error, unequal development in the three layers or fog either from processing or age.

Whatever its cause, it is frequently desirable to introduce some correction, even partial, although the manufacturers do not approve of the user taking too many liberties when handling their films.

The correction of a colour cast can sometimes be carried out by slight *local staining* but this destroys the purity of the whites for there are no dyes available which fix themselves only on the image dyes.

Only *chemical reduction* can give results which are of interest. Tests should first be made on scraps of film to determine the action of *weak acids* such as citric acid and *strong acids* such as dilute sulphuric or hydrochloric acid, of weak bases (borax) or strong ones (carbonate or caustic soda), of *oxidizing agents* (hydrogen peroxide, persulphates, sodium peroxide, acid dichromate), of reducing agents like sodium hydrosulphite at various pH values; of *sulphiding agents* such as sodium monosulphide and of *metallic salts* such as copper sulphate in acid, neutral, and ammoniacal solution. For each test note the concentration, the pH and the treatment time. Sometimes rinsing must be brief to leave, in the layers of the film, part of the correcting product (borax for example).

By way of example, several formulas will be given which have been disclosed for certain types of film. In view of the continual changes made by manufacturers in the constitution of their colour couplers, the information below has not an absolute value.

The resulting colours may vary with the type of film.

(The treatment time in all these solutions is 1–4 minutes.)

Cyan reducers

1% hydrosulphite. The action of this bath is increased as the pH is reduced. With Kodachrome images the magenta layer is reduced more rapidly than the others.

1% sulphite + a few drops of HCl until the pH is 7.

3% hydrogen peroxide: 10 cc + ·4% caustic soda 60 cc.

0·2% sodium peroxide.

Acetanilide 0·4 + sodium carbonate 0·2 + water 100.

Acetoacet-sulphanilide 0·1 + ammonia 10 + water 100.(93)

Reduction of blue and magenta by formation of greyer dyes.

Copper sulphate 1 + water 100 + ammonia 1·5. The action of this bath is less energetic in neutral solution. With some films, copper sulphate reduces the yellow.

Magenta reducers

Dry bisulphite 5 + sulphite 18 + water 1000 (pH 6·9).

m-aminobenzoic acid (hydrochloride) at a concentration of 0·75%, then 3% borax.

0·2% hydrazine sulphate. If the cyan and magenta images fade at the same time the cyan can be restored by immersion in 5% carbonate.

18% tartaric acid or 2% hydrochloric acid, then an alkali bath. With some films a magenta image is, on the contrary, intensified in an acid bath.

Yellow reducers

Caustic soda 3 + ferricyanide 20 + boric acid 1·5 + water 1000 (pH 11·8).

Cholic acid 5% (or sodium cholate).

Oxidation by chloramine (sodium salt of p-toluene sulphochloramine) 10 cc 1% + 1 cc 0·4% HCl. Does not keep.

Formalin 80 cc + 5% caustic soda 20 cc.

1% dichromate + 2 cc sulphuric acid then 5% bisulphite (oxidation).

Reduction of yellow and cyan

First treat in: potassium iodide 2 + iodine 1 + water 100, then in 40% hypo.

Yellow intensifier

10% hypo 100 cc + nitric acid 10 cc + 500 cc water. Wipe off the sulphur which has deposited, if necessary, then immerse in a solution of 3% hydrogen peroxide made alkaline with ammonia (which does not keep).

Magenta intensification (with some films)

2% sulphuric acid.

Cyan intensification (with some films)

5% borax, rinse very briefly.

561. Alteration of images

The three colour images obtained by colour development can be altered in three ways.

1. *Bleaching* by sunlight or electric arc. The prints should be kept in an album. To some extent they can be protected against ultra-violet radiation with a cellulose acetate sheet.(94) The magenta is the most stable of the colours.

2. *Acidification* by the carbon dioxide in the air gives a change of hue. This can be brought back to its original state by immersion in 1% borax without washing.

3. *Oxidation* accompanied by heat and high humidity. This results in a yellow-brown fog and reduction of the image; particularly when the layers still contain some slightly soluble developer. The magenta and yellow azamethines hydrolize to colourless ketones which are turned brown by reoxidation.

The formalin stabilizing has the effect of tanning the gelatin and thereby reducing the humidity in the layer.

Varnishing reduces the risk of acidification and oxidation.

562. Colour developer analysis

The analysis of colour developers consists of determining the substituted p-phenylenediamine on one hand and on the other the auxiliary constituents. The estimation of the latter is carried out by the usual methods considered in Chapter X. The p-phenylenediamine can be estimated as metol (para. 126). Spectrophotometric estimation can give good results (cf. para. 125). The two following methods were studied by Meyer and Roth in the Agfa laboratories.(95)

Potentiometric titration with nitrite in acid solution. When the p-phenylenediamine is all diazotized, nitric acid is formed which quickly raises the potential.

$$R_2N{-}C_6H_4{-}NH_2 + 2HCl + NaNO_2 \rightarrow$$
$$R_2N{-}C_6H_4{-}NCl{\equiv}N + NaCl + H_2O$$

The developing agent must first be separated from its sulphonate in *alkaline solution* with a solvent which is not miscible with water. The sulphonate is estimated by the difference between the total estimation after extraction in *acid solution* and heating to remove the SO_2.

50 cc of developer together with 9 g of anhydrous potassium carbonate and 12–15 g of sodium chloride are shaken with 40 cc benzene. The aqueous layer is separated and again extracted with 20 cc of benzene. The benzene solutions which contain the developing agent base are mixed. This base is extracted from the benzene with 20% hydrochloric acid and it is with this acid solution that the potentiometric estimation with a 0·04N solution of

The reason for an *actual grey separation* is quite different. The grey is an integral part of the colour reproduction system, and can be applied to all photographic, motion-picture and photomechanical processes. Although the method is not in current use, the grey separation method is a considerable advance on all other methods of colour separation.

The grey separation consists in removing from the normal set of tricolour negatives, the *complete grey image* (from white to black), then, which is most important, to *subtract* this from the three negatives of blue, green and red. Printing colour positive copies is carried out by exposing and developing a *grey image* (in other words, black and white), and three *reduced colour images* in cyan, magenta and yellow.

In normal three-colour subtractive synthesis the *grey* results from the superimposition of *equivalent amounts of the three dyes*—cyan, magenta and yellow. Any unequal combination of these three produces a *non-neutral tint* which is, in fact, a *mixture of grey with one or two of the colours*. The synthesis of the colours then becomes a *heterogeneous two-colour* system in which the two colouring elements are not always the same. This can be readily seen from Fig. 101, para. 492. The advantage of such a method is obvious: the neutrality of the greys is ensured by the use of a perfectly neutral dye or pigment, and the colours are given by the minimum amounts of dye (which are unavoidably imperfect).

If in a particular area of the colour image, the amounts of superimposed dyes, presumed pure, are $Q_C + Q_M + Q_Y$, corresponding to the cyan, magenta and yellow respectively, and if, for example, Q_M is the least of the three, the *amount of grey* Q_G used in the formation of the tint will be equal to Q_M. The amounts of dye actually used to give the colour will be $Q_C - Q_M$ and $Q_Y - Q_M$. In the present example the dominant colour is a grey which is more or less saturated according to whether Q_G has a low or a high value. The three-colour synthesis in this case is therefore reduced to a grey image Q_G, a cyan $Q_C - Q_G$ and a yellow $Q_Y - Q_G$.

How is the grey separation obtained? The best way is to use three separate black and white separation negatives. For each area of the image it is the *densest negative of the three* which gives the grey, on the *grey separation positive* (or separation of the least positive densities). Now if the three separation negatives are simultaneously *scanned point by point* with three light beams, it is possible, with suitable apparatus, to select the corresponding weakest electric signal, which in turn is converted to a luminous signal to expose the grey separation positive. The *reduced separation positives* of the three colours are either obtained using the grey positive as a mask on the original negatives, or directly in the electronic apparatus used for extracting the grey, by selective subtraction. The corrected separation negatives can also be obtained directly by electronic means.

If a colour original is used, the task is more complex, for corrections to eliminate unwanted absorptions must be included (corrections corresponding to masks). Scanning is therefore carried out with coloured light beams.

Printing colour images using a grey analysis was studied by the writer in 1935. Murray, Hall and Morse have also invented electronic apparatus to separate and correct the various images. Another method for dealing with transparencies has been perfected by Springdale Laboratories.(8) The original transparency is mounted on a transparent drum, whilst the four unexposed films are placed on a steel drum with the same axis. Scanning is carried out on a spiral track whose width is 50–100 μ. In addition to the systems for analysing, filtering and measuring the light beams, an electronic brain is used to resolve the various calculations.

To obtain the grey analysis, Yule(9) has given a further method, which is to print three *very contrasty separation positives*, and then copy them on to a single emulsion developed to a low contrast.

526. Contrast masks

It is sometimes desirable to reduce the excessively high contrast of some multilayer films. This is done with a contrast mask, preferably unsharp, having a density range about 25% of that of the original. The contrast mask is registered with the latter for printing the normal masks.

For duplicating saturated colour transparencies whose γ is 1·6–1·8, a mask with $\gamma = 0{\cdot}4$ and maximum density 0·5 is used. The γ is thus reduced to 1·2–1·4. During the preparation of the duplicate, the emulsion of the latter is in contact with the back of the original registered with the mask.(10) 10

Motion picture negative films can be corrected with a mask γ 0·3 (obtained on interpositive from the same negative without using filters).

The following method has been given for *Agfacolor* films:(11) the negative is developed in complementary colours to a γ of 1, instead of 0·65. The silver is rehalogenized and the sensitivity of the film is partly restored in a bath of sulphite. The emulsion face is exposed to red light, and the bottom layer is developed with a glycin developer containing a little potassium iodide (or an imidazole derivative) which converts the upper layers to undevelopable complexes. Maximum mask density: 0·6–0·7.

Highlight mask. The highlight mask is obtained from a *transparency*. It is developed to a low γ, and the density should not exceed 0·3. Together with the transparency, it suppresses the highlights; with the corresponding negative, it accentuates them.

Shadow mask. The shadow mask is obtained from a *negative*. Density 0·2–0·3. It reduces the contrast of the shadows on a negative, whilst it increases the contrast on a positive.

526b. Correction with fluorescent pigments

This method, evolved by Murray, is applied to the reproduction of coloured pictures and charts. Perfected by Yule, it is based on the following principle:

An image will be correctly reproduced if each original colour is altered in advance in such a way that the changes resulting from process imperfections are compensated. The same result can be achieved without altering the pigments themselves *by incorporating fluorescent substances in them.* This substance is almost invisible in white light, but is made visible by excitation with ultra-violet.

The pigments of the water-colour type are sold in tubes, and a suitable fluorescent substance is added to each. The artist must only mix them according to the manufacturer's instructions, otherwise false colours may be seen. The photographic analysis which follows painting is quite complicated, and must be carried out in accordance with the recommendations supplied, as ordinary three-colour filters are unsuitable.

In the same category as this method are the fluorescent pink, blue and green drawing inks for preparing multicoloured drawings and graphs. The blacks are made with Indian ink.

Among the fluorescent substances which have been disclosed(12) are pure chrysene (violet), impure chrysene (blue) and naphthacene (green).

The ultra-violet rays can be absorbed with two Wratten 2B filters.

SENSITOMETRY OF COLOUR IMAGES

527. Spectrosensitograms

A study of the *colour sensitivity* is very important (see para. 473–479), for which a spectrograph is essential. This can be constructed to produce *spectrosensitograms.*

The Evans *spectrosensitometer* is the best known:(13) the dispersing system is a moulded grating, whose spectrum is projected on to a slit, then on to the sensitive layer. A shutter disc and a revolving disc are used for the sensitometric exposures. The luminous energy received is measured with a thermocouple connected to a galvanometer, which enables the sensitivity to be expressed by the reciprocal of the number of ergs per cm^2 required to produce a given density.

The Morrisson and Hoadley *spectrosensitograph*(14) is derived from the Evans and the van Cittert(15) instruments. It enables 10 spectra to be printed whose exposure increases on a factor 2 scale. The light beam from a 7·5 A 6·5 V lamp is reflected by a mirror, collimated, intercepted by a 570 lines/mm grating; it is then reflected by a second mirror, projected on to a slit, reflected on to a third mirror and collimated before passing through a second grating, to be finally focused on to the exit slit combined with a sector disc rotating at 4000 r.p.m. A moving holder enables the complete spectrum to be traversed in 135 seconds.

528. Absorption spectrum

The first operation in any systematic study of sensitive materials for the production of colour images is the printing of the *sensitometer strips.* The various methods used for this were described in Chapter XV, para. 220. We would only remark that the exposure conditions (intensity, duration and colour temperature) should as nearly as possible be those encountered in practical use: variable intensity and constant time of about 1/50th second.

A developed and coloured sensitometer strip can give a *series of absorption spectra* whose determination enables the behaviour of the primary pigment used, to be seen.

The spectral transmission curve of a substance is the reverse of its absorption curve.

When a radiation of wavelength λ passes through an absorbing medium, of thickness d

$$\frac{I}{I_0} = e^{-Kd}$$

where I_0 is the intensity of the incident radiation, I that of the transmitted part and $\frac{I}{I_0}$ the *transmission coefficient.* K is the *specific absorption coefficient* for the radiation under consideration and e is the Naperian logarithm base, 2·718. The intensity of a radiation passing through an absorbing medium decreases exponentially, following the thickness (*Lambert's law*). The preceding formula can be written:

$$\frac{I}{I} = e^{-iCd}$$

when the substance is dispersed in a solvent or a transparent support (*Beer's law*). The absorption coefficient K is therefore proportional to the concentration C

$$K = iC$$

if the concentration is expressed in gram-mols of the substance per litre, the constant i is called the *molecular absorption constant.*

To draw an absorption curve, the wavelengths are plotted on the abscissa, and the coefficients of absorption or their logarithms on the ordinates.

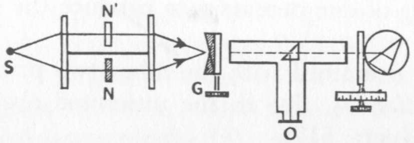

FIG. 112. Fery spectrophotometer. The two areas to be compared are examined at 0. The test solution is placed at N and balance is achieved by moving the wedges, G.

Measurements are made with a *spectrophotometer* in which the proportion of incident monochromatic flux passing through the coloured layer is measured. The monochromatic light beam is not produced with a filter, but with a prism (although narrow band interference filters can be used). An absorption compensating device enables the studied sample to be compared with a known density. This can be done with absorbing wedges, as with the Fery spectrophotometer (Fig. 112) or with nicol prisms as in the Konig, Martens and Grunbaum instrument, or even with shutters or rotating discs.

The receiver can be the eye or a photocell: the Yvon, Fery and Pulfrich instruments are visual; the Hardy, Boutry-Gillod, and Barton and Yoe ones are photoelectric. The latter is a 'zero' instrument: it comprises a monochromator whose light beam is divided between two barrier cells. A rheostat is used to balance the circuits.(16) Many other spectrophotometers are available.

A method of automatically recording the transmission curve is to expose panchromatic plates of *known sensitivity* in a grating spectrograph, in front of whose slit the coloured layer is placed. A neutral wedge is placed between the slit and the layer, or is fixed in front of the plate, to graduate the luminous intensity. Instead of using a wedge, a number of plates can be exposed for varying times or, better, one exposure can be given, and the density measured with a recording microdensitometer. The resulting values of transmission are then multiplied by the coefficients of colour sensitivity of the plate, corresponding to each wavelength. The figures which are finally obtained are not as exact as those obtained with a spectrophotometer, but two dyes can be readily compared to a first approximation.

529. Absolute density of coloured layers

The density of a coloured layer can only be actually measured with *complementary light*. Thus

A cyan layer is examined in red light;
A magenta layer is examined in green light;
A yellow layer is examined in blue light.

There are two cases which can be considered, depending on whether a single layer is measured, or whether the three single images are superimposed, and it is important that the two should not be confused.*

A *single layer* measured in complementary monochromatic light gives the pure or *absolute density* d_λ. If K is the coefficient of absorption—always less than 1—the quantity of dye necessary to produce the density d_λ is proportional to d_λ/K.

The same image, examined with the other two primary lights, gives the two *unwanted densities*, δ_λ, due to the unwanted absorptions, that is, the chromatic impurity (para. 517).

Thus the three primary images will give:

$$\begin{array}{llll}
\text{Cyan:} & d_R & \delta_G & \delta_B \\
\text{Magenta:} & d_G & \delta_R & \delta_B \\
\text{Yellow:} & d_B & \delta_G & \delta_R
\end{array}$$

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* *Translator's note*

There appears to be no definite correspondence between the absolute and total density used by M. Glafkides with the commonly used terms *analytical* and *integral* density used in English.

529b. Equivalent density

With a *multilayer* colour image the observed densities are always due to the group of three superimposed images, which mutually affect each other's purity. In the regions where only one layer is developed, then its measured density is the absolute density. In the majority of areas, however, this image is accompanied by a certain amount of the other two dyes which have unwanted absorptions in the spectral region of the other.

Suppose we have three primary images containing appropriate amounts of dye so that the resulting tint in *white light* of a given colour temperature is *neutral grey*. If the density of this grey is D_T, then

$$\begin{array}{lllllll}
D_{TR} = d_R & + & \delta_{Rm} & + & \delta_{Ry} & & \text{in red light} \\
D_{TG} = \delta_{GC} & + & d_G & + & \delta_{Gy} & & \text{in green light} \\
D_{TB} = \delta_{BC} & + & \delta_{Bm} & + & d_B & & \text{in blue light} \\
\multicolumn{1}{|c|}{\text{cyan image}} & & \multicolumn{1}{c|}{\text{magenta image}} & & \multicolumn{1}{c|}{\text{yellow image}} & &
\end{array}$$

where δ_{Rm} and δ_{Ry} are the unwanted images in red light given by the magenta and lower layers; δ_{Gc} and δ_{Gy} the unwanted images in green light from the cyan and yellow layers; δ_{Bc} and δ_{Bm} the unwanted blue light images from the cyan and magenta layers.

The density D_{TR}, or D_{TG}, or D_{TB}, in white light of known colour temperature, but corresponding to an examination in red, green or blue light, represents the *total density*, also called combined density, practical density and more frequently *equivalent neutral density*. It is equal to the sum of an absolute density and two unwanted densities.

The equivalent density of a primary image is therefore the density of grey obtained by superimposing sufficient amounts of the other two dyes. It is necessarily greater than the absolute density.

The ratio of an unwanted density to the principal absolute density of one image is a constant value, for example $\delta_{BO}/d_R = 1/4$. By replacing the values of the unwanted densities in the above equations by those of the corresponding absolute densities modified by a suitable coefficient, we can calculate an absolute density, after having measured the equivalent density, and knowing the amounts of the other two images voluntarily introduced to obtain a neutral. Conversely, it is possible to calculate the equivalent densities after measuring the absolute densities, which is more useful. This calculation is sometimes performed electronically.(17)

530. Measurement of colour densities

The measurement of the densities of coloured layers is carried out with different instruments depending on whether the absolute density, or the equivalent density, is required.

(*A*) *Measurement of absolute densities:* The monochromatic light required for absolute density measurement can be obtained by a monochromater, or by a series of colour filters.

Lapley and Weiss colour densitometer.(18) This is a combination of a Coleman double monochromator and a Western Electric densitometer. The dispersing system consists of two transparent gratings. As the spectrum is focused on a slit, the wavelength can be selected by rotating a cam. An interrupter disc with 15 radial slits rotating at 1800 r.p.m. feeds a 450-cycle signal to the amplifier. The light passing through the sample is received by an electron multiplier cell.

The colour densitometers using filters are more numerous than those with monochromators. A refinement is to replace the customary colour filters by interference filters(19) with very sharp absorption bands.

To make an approximate determination of the density of a monochromatic coloured area, place it alongside a calibrated density scale, and illuminate it with a diffuse source of the complementary colour. The comparison density scale must have similar graininess to the test.

Behrendt colour densitometer.(20) This uses a 25 W lamp, a condenser with an iris diaphragm, and a filter disc having an 8 mm Schott BG 19 infra-red absorbing filter in addition to three 2 mm filters of Schott BG 12, red; VG 9, green; and RG 2, blue. The light is received by a barrier photocell and measured with a galvanometer.

Thiels colour densitometer.(21) The filters are mounted concentrically on a rotating disc and successively receive the light reflected by a movable prism, which is then transmitted to a lens. The light beams passing through the film are received by a photocell connected to an amplifier. The blue component is carried in one direction to a galvanometer, whilst the green and red are connected in reverse. The measurement of the three densities is given by the displacement of the two reflecting prisms. The equivalent density is obtained by combining the absolute and unwanted densities.

Sweet colour densitometer.(22) This instrument is designed to overcome the fatigue of photomultiplier tubes. It consists of a 6 V lamp, a condenser, two infra-red absorbing filters and a cell surrounded by a cylinder holding six filters. The three curves of a sensitometer strip are plotted in less than two minutes in three inks of different colour.

Herrnfeld colour densitometer.(23) The light, at 3000°K, from an 8·5 V 4 A lamp is condensed on an aperture fitted with an infra-red absorbing filter (Corning 9780, 2·5 mm) in front of which is an interrupter producing 360 c.p.s. A further disc, containing four filters is placed between this aperture and a lens which focuses the light on to the film. An integrating bar of transparent plastic material receives the diffuse light which is taken to a cell and an amplifier.

Eastman 31A electronic colour densitometer.(24) A lens A receives the light from a 100 W lamp and forms an image on lens B. After reflecting with a mirror the image is projected on to the film, followed by a photocell. A second similar cell receives the comparison beam from the lamp.

Frayne and Jacobs colour densitometer.(25) The Westrex model R.A. 1100 E, uses a selenium photocell which receives almost all the diffuse light.

(*B*) *Direct measurement of equivalent density.* These densities are measured by superimposing on the sample area, 2 or 3 *coloured wedges* made up of th same dyes as those of the film considered. A supplementary grey wedge is used to balance the system: *R. M. Evans*(26) and *Schneider and Berger*(27) instruments are of that type.

Heymer and Sundhoff colour densitometer.(28) Two identical beams are viewed simultaneously. The sample is placed in one path and one to three colour wedges are in the other.

(*C*) *Pavelle colour densitometer*(29) *for printing control.* The light from the source is filtered through $CuCl_2$ solution to remove the infra-red, and is condensed on to a cell connected to an amplifier and an oscilloscope. A disc rotating at 300–900 r.p.m. contains 3 filters in sectors with transmission maxima at 440, 540 and 660 mμ. Neutral densities enable the light passing through the three filters to be balanced. By introducing a coloured area, a wavy line is produced on the oscilloscope screen. This can be straightened by introducing three filter discs, each containing 14 filters of the same type as the film dyes.

(*D*) *The measurement of paper densities* by reflection is generally complicated by surface reflections.

531. Colour balance

To achieve colour balance together with sufficiently accurate colour reproduction in the subject, several rules must be adhered to, and this is not always easy to accomplish in practice.

(*a*) The *colour sensitivity* of each layer of the negative material must be exactly established in order to make the analysis under the most favourable conditions.

(*b*) The *speed* of each negative layer, which differs with its position in the film, must balance that of the others.

(*c*) The *development* of the three separation negatives must be carried out to the same gamma, or to an equivalent gamma if a correction stage is introduced.

(*d*) If *masks* are used, they must be prepared with the greatest care or the results will be worse than if they had not been used.

(*e*) The *primary dyes* must be of the greatest possible colour purity. They are the source of many inaccuracies.

(*f*) The *average density* of each colour image must be carefully controlled, with respect to the colour temperature of the source, by standardizing the printing time and by ensuring correct development. A colour image which is too dense results in an overall colour cast.

(*g*) The three images which make up the final image must have the same *contrast* and the same shape of characteristic curve (by measurement of the *equivalent densities*). When the three images have the same contrast, the greys appear well balanced.

The importance of correct grey scale reproduction has been contested.(30) It is true that good grey reproduction does not necessarily mean that colours will be reproduced faithfully, for the adjustment of the three images to give good grey reproduction will not eliminate the unwanted absorptions of the image dyes. However, if the curves of the three images are not coincident, the situation will be even worse. The achievement of a grey scale is a sign of correct balance and careful work. Moreover, an image whose greys are coloured is not generally pleasing.

532. Taking colour photographs

As the exposure latitude of colour emulsions is small, errors must not be made as they are impossible to correct. The first thing, therefore, is to choose the main subject in the scene (from the visual point of view), and after measuring its average brightness, attempt to expose so that it is in the middle of the negative characteristic curve. If the subject has a brightness range which exceeds the acceptance of the negative, then it is necessary to decide which parts of the subject must be recorded and which can be lost.

The incident light necessary for photography with a 'daylight' type negative film ASA index 16 is about 500 sq. ft. candles at an aperture of f 2 and at 24 frames per sec. With the newer materials of higher sensitivity 300 sq. ft. candles is enough.

For ordinary photography, satisfactory results are obtained with summer sunlight with an exposure of 1/50th sec. at f 6·5 (16 ASA or 13/10 DIN film). Exposure should be increased under the following conditions:

	Multiply by
Light cloud	2
Overcast sky	4
Dull heavy cloud	16
Winter	2
Shaded subject	8
Brilliant subject	Divide by 2

In artificial light, two 500 W lamps in ordinary reflectors (100 hour over-run lamps) at 10 feet from the subject enable exposures of 1/5–1/10 sec. at f 2 to be given.

For considerations of light sources, refer to Chapter XXVI. In the studio, daylight can be imitated with arc lamps corrected by a bluish filter (Brigham Y1 for example), or by filtered tungsten lamps.

A film balanced for 3400°K tungsten light can be used in daylight with a Wratten 85 filter.

Some negative films can be used with any light source without filters, corrections being made during printing.

In all cases avoid excessive brightness range; side lighting, shadows on the face, subjects partially in the shade and *contre-jour* effects.

Auxiliary exposure. The latent image of colour films can be intensified considerably by low intensity long duration post exposure until an extra 0·1–0·2 fog density is obtained. Three groups of light sources are used, each with a different colour filter.(31) Exposure time with Eastman Color: 20–30 minutes; film speed, 20 feet per minute. Blue filter = Wratten 213 + 47, green filter = 61 + 16, red filter = 70. 10 W lamps having an emission surface of 4–10 cm².

By latensification with post exposure the exposure time can be reduced 2–4 times. A reduction of 6 times has even been claimed for Ektachrome film.(32) Exposure time 1–2 secs. at 60 cm with a safelight containing a 7 W pearl lamp and an aperture 25 mm diameter. An orange Wratten G filter, a neutral density of 1 and if necessary a blue-green or pink correction filter are used. First development 18–20 minutes at 21°C. Leave 8 minutes in the colour developer before fogging, which is the least to reverse the film, followed by a further 7 minutes' development.

533. Measurement of subject luminosities

There are several exposure meters which measure the average subject brightness. For precision work, however, it is advisable to measure the *extremes of brightness*. For this, the subject can be compared with the extinction of a filament (Volomat apparatus, Paris) or a telescope photometer can be pointed successively at the shadows and highlights of the scene. The brightness of the deepest shadow to be recorded is important for exposing negative materials, whilst for reversal films, it is the brightness of the brightest necessary highlight which must be determined.

An important point which is frequently neglected is the measurement of the brightness of actors' faces in scenes of known brightness range. The ratio of this brightness to the brightness of the decor is a vital factor in the balance of the colour image, and in the print-making process.

'Norwood Director' exposure meter. This instrument comprises a hemispherical receiver of opal glass which is placed in the position occupied by the subject to be photographed. As the light is gathered from all directions, the effective illumination is recorded. A second receiver of clear glass enables the brightnesses to be measured, the instrument being pointed towards the control area. A perforated mask also enables the part played by each lamp in the total illumination of the subject to be determined.(37)

For colour temperature measurement see para. 451.

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1. Miller T. H.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1949, 133–155.
2. F.P. 836,444.
3. Watter O.: *Zeits. Wiss. Phot.*, Dec. 1953, 228; *Sci. et Ind. Phot.*, 1954, 160.
4. *J.O.S.A.*, 1952, 402.
5. Note by L. P. Clerc in *Le Procedé* in an arrangement of the *Bulletin for Graphic Arts* No. 8 (1946) and No. 11 (1948).
6. Yule J. A. C.: *J.O.S.A.*, 1940, 322–331 (second part).
7. F.P. 834,838 (1937–38); 871,370 (1938–39). See also I.G.F. F.P. 873,706 and C. Add. 53,622 (1943–44).
8. *Photo. Engr. Bull.*, May 1950, 13.
9. Yule J. A. C.: F.P. 867,412 (1939–40) and *J.O.S.A.* 1940, 322 (Part 1).

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10. Loessel E. H. (Ansco): *P.S.A. Jl.*, 1949, 14.
11. Zeh, Clever and Watter: *Bild u. Ton*, 1950, 315–319; *Sci. et Ind. Phot.*, 1951, 30.
12. Yule J. A. C.: F.P. 917,585–6 (1940–43).
13. Evans C. H.: *J.O.S.A.*, abstracted in *Sci. et Ind. Phot.*, 1940, 152. Jones and Sandvik had previously constructed a spectrosensitometer composed of a monochromator and a rotating disc: *Sci. et Ind. Phot.*, 1921 (1), 127.
14. Morrison G. A. and Hoadley H. O.: *P.S.A. Jl.*, 1950, 64–69.
15. Van Fittert: *Rev. d'Opt.*, 1923, 57.
16. Barton C. J. and Yoe J. H.: *Ind. Eng. Chem.* (Anal. Ed.) 1940, 166.
17. Bingham used the matrix calculation. *Sci. et Ind. Phot.*, 1946, 301.
18. Lapley A. C. and Weiss J.P. (Dupont): *Jl. Soc. Mot. Pic. Tel. Eng.* 1951, 23–29.
19. Letzer E. K. and Powers S. A.: *J.O.S.A.* 1954, 870.
20. Behrendt W.: *Veroff. Wiss. Photo-Labo. Agfa*, 1951, 32–36.
21. Thiels A. F. (Gevaert): *Jl. Soc. Mot. Pic. Tel. Eng.*, 1951, 13.
22. Sweet M. H.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1950, 35–62.
23. Herrnfeld F. P.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1952, 184–190.
24. *Jl. Soc. Mot. Pic. Tel. Eng.*, 1953, 696–708.
25. Frayne J. G. and Jacobs J. H.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1955, 67–71.
26. Evans R. M.: *Sci. et Ind. Phot.*, 1938, 340.
27. Schneider and Berger: *Sci. et Ind. Phot.*, 1944, 316.
28. Heymer and Sundhoff: *Sci. et Ind. Phot.*, 1938, 22.
29. Varden L. E.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1951, 197–204.
30. Williams F. C.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1951, 112.
31. Carey K. M.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1954, 61.
32. Eyerman J. R. (Life): *Photography*, 1953, 50 and 206–209.
33. Woolsey R. A.: *Jl. Soc. Mot. Pic. Tel. Eng.*, 1947, 548.

Chapter XXX

COLOUR DEVELOPMENT

534. Theory of colour development

The formation of coloured images by colour development was disclosed in 1906 by Homolka. In 1912, R. Fischer tried to obtain three coloured images in blue, magenta and yellow simultaneously in three superimposed emulsion layers. His experiments were not successful, due to the diffusion of the colour couplers into neighbouring layers. This difficulty was not overcome until much later, by means of several different devices which will be examined in the following paragraphs.

The organic compounds, or systems of organic compounds, which can form *coloured pigments or dyes* when oxidized by the latent image are very numerous. Fischer drew up a fairly complete list of types.

Once the colour image has been produced, the *accompanying silver image must be dissolved* to reveal the true dye image.

Colour development takes place when a latent image is developed with an unsymmetrical *dialkyl-p-phenylenediamine* in the presence of a *phenol* or a compound containing a *reactive methylene group* CH_2. The phenylenediamine is the developer, and the phenol (or reactive methylene compound) is the coupler or former.

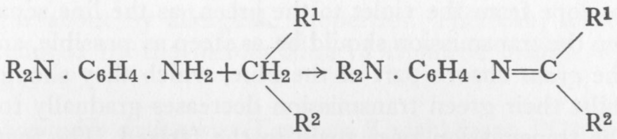
The most common dialkyl-p-diamine is diethyl-p-phenylenediamine (or p-diethylamino-aniline). By *oxidizing* in the presence of 1-naphthol, an insoluble blue indophenol is produced, following the reaction:

$$(C_2H_5)_2N\,.\,C_6H_4\,.\,NH_2 + C_{10}H_7OH \rightarrow (C_2H_5)_2N\,.\,C_6H_4N{=}C_{10}H_7{=}O$$

p-diethylamino-aniline 1-naphthol Indophenol

For the reaction to take place, the para position of the naphthol is free, or is occupied by a displaceable group.

If the coupler is a reactive methylene compound with the formula $R'-CH_2-R^2$, the reaction is:



$$R_2N\,.\,C_6H_4\,.\,NH_2 + CH_2\!\begin{smallmatrix}R^1\\R^2\end{smallmatrix} \rightarrow R_2N\,.\,C_6H_4\,.\,N{=}C\!\begin{smallmatrix}R^1\\R^2\end{smallmatrix}$$

p-dialkylamino-aniline Methylene coupler Azamethine dye

B	Water to	1000 cc
	p-nitrophenylacetonitrile	1 g

Many other colour developing solutions can be used (see following chapter) including those using a sulphamido-diamine developer, which are non-toxic.

*Alkaline stop bath S*13-9*a*

Water to	1000 cc
Sodium carbonate anh.	50 g
Sodium sulphite anh.	50 g
Potassium bromide	200 g

Dilute with 9 volumes of water. Time 4 minutes.

*Bleach bath R*13

Water to	1000 cc
Sodium sulphate anh.	100 g
Sodium carbonate anh.	12 g
Potassium ferricyanide	20 g

Treatment time 2–3 minutes followed by fixing.

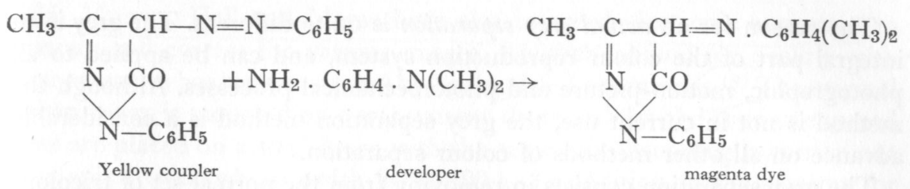
523. Masking with coloured couplers

The most practical method of automatically compensating for the imperfections of negative dyes is by means of coloured couplers, elaborated by Hanson and Vittum. The principle is to convert the unwanted absorption image of the single colour image to a uniform layer of this colour over the whole image, which is done by colouring the transparent parts with a dye which absorbs precisely those wavelengths which are insufficiently transmitted by the image dye.

The correcting effect is carried out by using *coloured couplers* which lose their colour when they combine with the developer. If, for example, we have an orange coupler which on development gives a cyan dye, the final image will be orange in the low densities and cyan in the high densities: the inefficient green transmission will then be spread evenly through the layer, having no effect but to increase the exposure time.

The coloured coupler correction process is used in the *Ektacolor* and *Eastman Color* films (cf. para. 517) where the emulsion which gives the cyan image (red record) contains an *orange* coupler, and the layer which gives the magenta image (green record) contains a *yellow* coupler. The yellow colour corrects the inadequate blue transmission of the magenta dye.

The coloured couplers are obtained by attaching to the colourless coupler a chromophoric group which can be split off by combination with the oxidized developer by rupturing the link. Thus a yellow coupler for the magenta image can be prepared by attaching the group $-N = N - C_6H_5$ to the reactive methylene group of the original coupler.



We have already shown the proportions of unwanted absorptions in Ektacolour film (para. 517). Although relatively small, they are still present, and for photomechanical reproduction it is recommended that the magenta separation should be masked. To obtain this mask, a panchromatic emulsion is exposed under the original negative first to blue light (Wratten 47 + 39A filters) then to red light (Wratten 70). The ratio of the two exposures is 2:3 ($\gamma = 20$–25% of the original). The magenta separation positive from the original plus the mask, is made with a Wratten 61 green filter to which is added a density 1 neutral filter, if the yellow separation positive is made with the 47 + 39A filters and the red separation with the 70 filter.

The separation positives thus prepared can be used to prepare screen negatives. A *black printer* must be added to them.

524. Black record

There are several methods of obtaining the black image used for photomechanical printing.

(*a*) *Use of a dense yellow filter*. The image is underexposed but completely developed.

(*b*) *Copying with three successive exposures* through blue, green and red filters. That made through the red filter is increased by 50%. Some people, on the contrary, prefer to expose much less to red light. Everything, in fact, depends on the density of the filters, the colour sensitivity of the emulsion and the nature of the subject.

(*c*) *Mask method*. A *temporary mask* is first prepared from the original negative with two partial exposures using blue then green filters. The minimum density should be 0·3 and the density difference the same as that of the Ektacolor measured in red light. The pack (original plus temporary mask) is copied with red light so that the *new mask* has a minimum density of 0·3 to 0·4 and a gamma of 1·6 to 1·8. By superficial reduction, the minimum density is reduced to 0·1. The black positive is obtained with this second mask combined with the original, using the deep red Wratten 70 filter. There must be no strong colour contrasts.

A theoretical study of the black image has been made by Yule.(6)

525. Actual separation of greys

The 'black printer' such as the one indicated above is only a device for covering up the imperfections inherent with three-colour half-tone. It has nothing in common with a true photographic separation.

50% lower than that of A; and for the yellow separation, a combination of A′+B is used.

520. Masks on two layer films

In blue and green light, there are usually two unwanted images. Those in blue light come from the cyan and magenta images, whilst those in green light come from the cyan and yellow images. To avoid superimposing two separation masks, a film having two superimposed layers can be used, sensitive respectively to red and green and to red and blue, or more simply to red and to blue and green for the two pairs of masks. It is, however, necessary to have different contrasts for the two emulsions.

The *Agfa 'Kombi films* invented by Hickethier have two superimposed emulsions as above, with the difference that each layer contains a colour coupler giving coloured masks.

Separation in	Negative image	Colour of Kombi film images
Blue light	Yellow	Magenta + cyan
Green ,,	Magenta	Cyan + yellow
Red ,,	Cyan	Yellow + magenta

No filters are necessary for making these masks, as separation is carried out by sensitizing the layers.

Masked negatives on two-layer films. Carroll and Staud(2) suggested the use of a separation negative material of silver chloride having a second emulsion on the surface of silver bromide, for printing the mask. After development and oxidation of the surface image with quinone in isopropyl alcohol, the silver chloride is removed with sulphite solution saturated with silver bromide, and the film is fogged and redeveloped to a positive, the residual bromide giving the mask.

Watter(3) has described films having an emulsion for producing the separation negative, and an emulsion containing an orange azo coupler for the mask. On colour developing, the coupler produces a blue dye, transparent to the printing light. The residual orange coupler acts as a positive and therefore constitutes a mask. The masking layer for correcting the yellow is sensitive to green and red, whilst the masking layer for correcting the magenta is only sensitive to red.

Masking by supplementary exposure of long duration and low intensity. Maurer and Yule(4) have suggested the possibility of forming on the negative latent image a positive image serving as a mask, by prior exposure of long duration and low intensity. If the supplementary exposure is given after the main exposure, the solarizing effect does not occur; on the contrary, the latent image is intensified. Furthermore, readily solarized emulsions which show particular reciprocity failure are needed.

521. Unsharp masks

Masks have the disadvantage that they produce an *edge effect* on the image. This defect is overcome by using unsharp masks. The unsharpness reduces the overall contrast, but not that of the fine detail. It eliminates errors in registration and consequently gives better detail than a sharp mask, contrary to what one would think.

The unsharpness can be produced in two different ways:

(*a*) By interposing a translucent sheet about 0·75 mm maximum thickness.

(*b*) By interposing a transparent sheet (or even the base of the original) about 0·2 mm thick at the most, and rotating the pack on a turntable, the lamp being 1·8 m above and 0·6 m off the axis. The image is bigger than the original if the lamp is too near. To some extent shrinkage of the base counteracts this enlargement.

522. Magenta coloured masks

Sharp masked negatives are prepared in the cameras used for *photomechanical* reproduction with masks developed to a magenta colour. These masks are mainly used when the image is to be enlarged, which avoids difficulties of registration. They reduce the gamma and increase the colour saturation.

The two masks are those normally obtained with a red filter (A, for the correction of the magenta image) and a green filter (B, for the correction of yellow image).

The exposure of each mask is made on a panchromatic plate placed in the screen holder of the camera. The mask is developed to magenta in a colour developer and then replaced in the holder. After this, the appropriate separation is made with the blue, green and red filters successively. For the separation of the yellow, the magenta-coloured mask B is used, whilst for the magenta separation mask A is used, and for the cyan, a clear glass sheet only.

The distance between the mask and the panchromatic plate is 3 mm. The emulsion must be soft, unless the document is too pale.

The masks must have a minimum density of 0·3 to 0·5. Gamma of A = 40–45% of the original; gamma of B = 55–65%.

If the masks are not developed to magenta colour, they must be made unsharp by interposing a diffusing film during their exposure.

When separating pictures for photogravure, there is no need to correct the cyan and black printer negatives.

It should be remembered that each original must be accompanied by register marks, a grey scale, and patches of each primary ink.

Magenta colour developing solution(5) (can cause dermatitis):

A	Water to	1000 cc
	Diethyl-p-phenylenediamine hydrochloride	18 g
	Sodium carbonate	40 g
	Potassium bromide	1 g